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SHORT RESEARCH COMMUNICATION

Original isotopic composition of water in precipitation by different methods

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Abstract Stable isotopes of ^{2}H and ^{18}O in precipitation are different globally and carry all information about water molecules movement in hydrosphere cycles. Isotopic composition is a function of temperature, relative humidity, and speed of evaporation at different latitudes, longitudes, and altitudes. On the basis of this, we observe local meteoric water line measurements in the plot of δ^2H versus δ^{18}O. It will be interesting to know the original isotopic composition (without any modification) in a transition from cloud down to earth in different environmental conditions. This had been done by plotting of slope versus intercept of Local Meteoric Water Line (LMWL) at different altitudes in different years of observations. Intercept of LMWL with Global Meteoric Water Line (GMWL) data taken from the hydrology frame work of Corsica was plotted and it was found that the isotopic composition of water in precipitation by all these methods is same.

Keywords Original isotopic composition · Hydrology · GMWL

Introduction

Stable isotopes of ^{2}H and ^{18}O are powerful tracers of the water molecules in the hydrosphere and water cycle. Stable isotope ratio between ^{2}H/^{1}H and ^{18}O/^{16}O is expressed by δ^2H and δ^{18}O, where δ is a sample ratio, and $\delta = (R_{\text{sample}}/R_{\text{SMOW}} - 1)$ 1000, where $R = {}^2$H/^{1}H or ^{18}O/^{16}O is taken standard sea mean ocean water (SMOW now VSMOW). One of the most important contribution had been made by Craig 1961 as a correlation of precipitation on global basis, between δ^2H and δ^{18}O, where $\delta^2\text{H} = 8\ \delta^{18}\text{O} + 10‰$. Later, $\delta^2\text{H} = 8.13\ \delta^{18}\text{O} + 10.13‰$ has given by Rozanski et al. 1993 and is taken as Global Meteoric Water Line. This gives the global distribution for stable isotopes in fresh precipitation. These are the injected tracers on global basis. Due to environmental conditions especially temperature and humidity, these isotopic composition is modified in different places in the region, and therefore, what we observe is modified local meteoric water line (LMWL). The slope and intercept for these LMWLs do depend on hydrological parameters.

The experimental results of plots on δ^2H and δ^{18}O had been discussed both theoretically and experimentally by various investigators Friedman 1953; Craig 1961; Dansgaard 1964; Yurtsever 1975; Singh and Kumar 2005. All these studies reflect the variation of slope and intercept on δ^2H axis on plot of δ^2H and δ^{18}O water in various stages of hydrological cycle. What we measure all the time is LMWL. Knowing LMWL can be found the isotopic composition without modification due to environmental condition, temperature, and humidity. This has been suggested by Singh (2013), and this study has been done from the data of Corsica.

Recently, Geldern et al. 2014 reported the stable isotopic pattern in a climate change and hydrology framework of Corsica. These extensive data, i.e., measurement of δ^2H and δ^{18}O at different altitudes, in different seasons, in lakes, spring, and streams, need further investigation by the method of plotting slopes versus intercepts of LMWL.

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The methodology adopted for interpretation of data for local meteoric water line (LMWL)

Global meteoric water line (GMWL) as available is based on precipitation, as well as, on global distribution of stable isotope in precipitation (Rozanski et al. 1993), where

$$\delta^2\mathrm{H} = 8.13\delta^{18}\mathrm{O} + 10.8. \tag{1}$$

Let us take the water with an isotopic composition of $\delta^{18}\mathrm{O} = -5, -7, -10, -15, -18$, and -20‰. We can find the corresponding value of $\delta^2\mathrm{H}$ to be –29.85, –46.11, –70.50, –111.16, –135.54, and –151.80‰, respectively, from Eq. (1). Let us take the isotopic composition of water for different slopes, for example, 7.4–8.1 [as found in the measurements of local meteoric water line (LMWL)] and calculate the intercepts by the equation:

$$\delta^2\mathrm{H} = \text{slope } (x \text{ axis})\, \delta^{18}\mathrm{O} + \text{intercept } (y \text{ axis}). \tag{2}$$

The intercepts thus calculated are given in Table 1, for different isotopic compositions and different slopes. The plots are given in Fig. 1 (Table 2) and have six different lines, i.e., 1–6 are straight lines corresponding to different isotopic compositions of water. Each line corresponds to different isotopic compositions of water on GMWL.

If we measure and plot $\delta^2\mathrm{H}$ and $\delta^{18}\mathrm{O}$ in different seasons in different regions with different environmental conditions, the average values for each site of the measurement will produce a flatter ellipse. If we plot $\delta^2\mathrm{H}$ versus $\delta^{18}\mathrm{O}$ for each site for each season separately, we can obtain different LMWLs in the region. Each plot will give us different slopes and intercepts, and on plotting the slopes versus intercepts, we get a straight line and we can find $\delta^{18}\mathrm{O}$ and $\delta^2\mathrm{H}$, as given in Eq. (2), which is the original isotopic composition of water in precipitation on GMWL. The combined plot giving flatter ellipse-type picture is the combination of many LMWLs. The slope of each LMWLs is very close to each other, but intercept on $\delta^2\mathrm{H}$ is separate and distinguishable as can be seen for different LMWLs.

It looks unusual that slope versus intercept plot is giving isotopic composition of water on GMWL, but if we look to the geometrical consideration, we get the answer. If we draw two lines making angle θ for the length say r, the separation between two lines shall be $r\theta$ and provided θ is small. If double the angle says 2θ, separation be $r2\theta$, and if we have 3θ, the separation will be $r3\theta$. The plots of 1θ, 2θ, and 3θ and separation of $r1\theta$, $r2\theta$, and $r3\theta$ shall be on a straight line. In this present analysis and observation of GMWL and LMWLs, the change in slope for each site is small; however, intercepts are large. This can also be seen from Table 1, and for slope ranges from 7.4 to 8.1, the intercepts are -3.8–10.2 for the sixth line. This is the basis of interpretation. So far in the literature, we did not find any consideration of intercept, but this analysis of slope versus intercept is a very useful tool to correlate experimental data of the region and get original isotopic composition of water in precipitation. Therefore, slopes and intercepts of LMWLs in a region are useful, as given above.

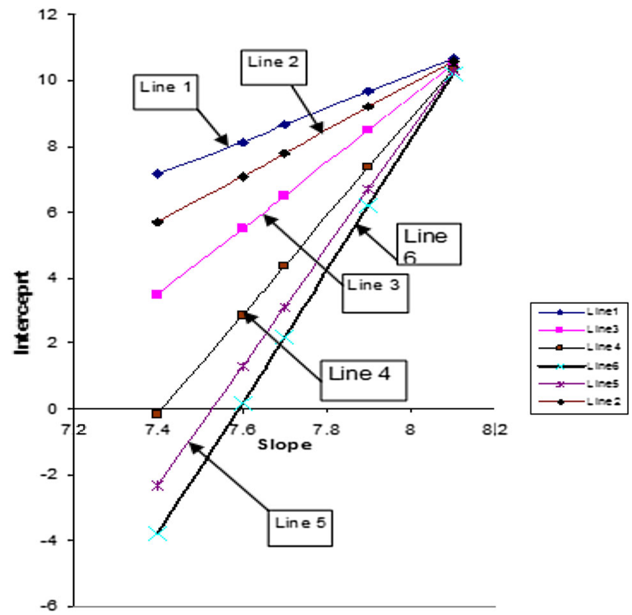

Fig. 1 Intercept on $\delta^2\mathrm{H}$ axis versus the theoretical values of the slope of $\delta^2\mathrm{H}$ and $\delta^{18}\mathrm{O}$ plots for different waters having $\delta^{18}\mathrm{O}$ from -5 to -20‰ corresponding values of $\delta^2\mathrm{H}$, as given by line 1 to line 6

Table 1 Slopes/intercept using relation $\delta^2\mathrm{H} = \text{slope } \delta^{18}\mathrm{O} +$ intercept for the water

Lines for different isotopic composition slopes	Intercept					
	1	2	3	4	5	6
7.4	7.15	5.3	3.5	−0.15	−2.34	−3.8
7.6	8.15	7.1	5.5	2.85	1.3	0.2
7.7	8.65	7.8	6.5	4.35	3.1	2.84
7.9	9.65	9.19	8.5	7.35	6.7	6.2
8.1	10.65	10.6	10.5	10.35	10.3	10.2

Table 2 Theoretical values of $\delta^{18}O$ and $\delta^{2}H$

Line No.	$\delta^{18}O$‰	$\delta^{2}H$‰
1	−5	−29.85
2	−7	−46.11
3	−10	−70.50
4	−15	−111.16
5	−18	−135.54
6	−20	−151.80

Experimental data

The island of Corsica situated in the North-Western Mediterranean basin between 41° and 43° latitudes, with a North–South extension of 183 km and a maximum of east–west extension of 83 km, has a moderate-to-rugged regular topology, with a maximum elevation of 2706 m. The annual precipitation is 600 mm/annum. Annual temperature decreases with altitude at the rate of −6 °C per km. At high altitudes, the temperature difference between the coldest and warmest months in mountain is about 20 °C. 166 samples were collected by Geldern et al. 2014 during the years 2003–2009 from rivers, lakes, and streams. The data obtained and reported in a chronological order are on different dates with details of location, elevation (altitude), temperature, latitude, and longitude along with a measured value of $\delta^{18}O$ and $\delta^{2}H$.

Interpretation and discussion

Method I: Geldern et al. 2014 measured values of $\delta^{18}O$ and $\delta^{2}H$ for the precipitation at different altitudes. We plotted, as given in Fig. 2 (Table 3), and the measurements of $\delta^{18}O$ and $\delta^{2}H$ at different altitudes of 10, 30, 50, 50, 100, and 100 m Above Sea Level (m.a.s.l.) and obtained LMWL to be $\delta^{2}H = 7.08\delta^{18}O + 4.17$‰. The range of altitude for this LMWL is 56.67. Similarly, we plotted $\delta^{18}O$ and $\delta^{2}H$ at different altitudes say, from 148 to 269 taking range of altitude to be 206.90 and obtained LMWL to be $\delta^{2}H = 6.29\delta^{18}O\text{-}1.88$‰. This has been done for all the different altitudes, as given in Table 4.

For the LMWL slopes and intercepts as given above, we plotted the slope versus intercept on $\delta^{2}H$ axis, as given in Fig. 3 (Table 5). These slopes versus intercepts are straight lines and as per interpretation, Eq. (2), the original isotopic composition on GMWL is as follows:

$$y = 9.03x - 61.13,\ \text{or}\ -61.13 = -9.03x + y,$$

$$\text{i.e.,}\ \delta^{2}H = -61.13; \delta^{18}O = -9.03.$$

Therefore, it can be taken to be original an isotopic composition of water which is modified at different environmental conditions at different altitudes. If this is so, then, we can take $\delta^{18}O = -9.03$‰, and if we multiply it with the slope of LMWL (as given above) and add to this value of $\delta^{2}H$ (as observed value as given above), we can obtain value of $\delta^{2}H$ (calculated), as given in Table 6.

It is to be noted that all the values are within the statistical error and within the range of −2.00‰, i.e., $\delta^{2}H = -61.13^{‰}$ (range −63.13 to −59.13‰). $\delta^{18}O$ and $\delta^{2}H$ measured at different altitudes are well correlated with each altitude and original isotopic composition of water in cloud formation and rains. We observe modified LMWL due to different environmental conditions and topological conditions of the surface etc. during the transit.

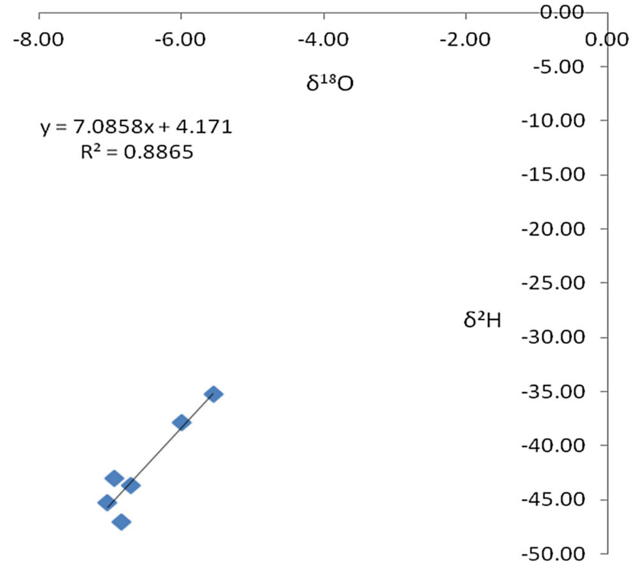

Fig. 2 Measured value of $\delta^{2}H$ and $\delta^{18}O$ with mean altitude

Table 3 $\delta^{2}H$ and $\delta^{18}O$ values at different altitudes with specific dates

Date	Altitude (m.a.s.l.)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
10-May-08	10	−6.85	−47.00
28-May-07	30	−6.00	−37.90
2-Jun-07	50	−5.55	−35.20
2-Jun-07	50	−6.95	−43.00
8-Jun-07	100	−7.04	−45.30
11-May-08	100	−6.72	−43.70
	340		
Mean	56.67		

Method II: Geldern et al. 2014 had given measured value of $\delta^{2}H$ and $\delta^{18}O$ during different periods in the years 2003–2009. The basic measured value of the data is given for the months of April–May–June for year 2003, May–August–October for year 2004, May–October for the year 2005, May–June–August for the year 2006, May for the

Table 4 LMWL at different altitudes

Altitude mean in m.a.s.l.	LMWL
56.67	$\delta^2H = 7.08\delta^{18}O + 4.17‰$
206.90	$\delta^2H = 6.29\delta^{18}O - 1.88‰$
439.38	$\delta^2H = 7.15\delta^{18}O + 3.86‰$
532.57	$\delta^2H = 7.99\delta^{18}O + 10.22‰$
661.25	$\delta^2H = 8.13\delta^{18}O + 9.01‰$
730.17	$\delta^2H = 7.32\delta^{18}O + 5.68‰$
876.89	$\delta^2H = 6.04\delta^{18}O{-}4.06‰$
920.43	$\delta^2H = 9.98\delta^{18}O + 27.85‰$
1026.92	$\delta^2H = 7.63\delta^{18}O + 8.37‰$
1152.44	$\delta^2H = 6.63\delta^{18}O{-}0.13‰$
1234.60	$\delta^2H = 8.37\delta^{18}O + 14.93‰$
1344.71	$\delta^2H = 7.05\delta^{18}O + 1.22‰$
1426.67	$\delta^2H = 5.63\delta^{18}O{-}11.31‰$
1555.26	$\delta^2H = 8.35\delta^{18}O + 14.23‰$
1741.78	$\delta^2H = 5.97\delta^{18}O{-}6.14‰$
1848.86	$\delta^2H = 5.80\delta^{18}O{-}10.53‰$
1933.75	$\delta^2H = 9.17\delta^{18}O + 22.17‰$
2075.67	$\delta^2H = 7.44\delta^{18}O + 7.35‰$
2319.50	$\delta^2H = 4.39\delta^{18}O{-}24.28‰$

Table 5 Slope and intercept at different altitudes

Altitude	Slope	Intercept
56.67	7.08	4.17
206.90	6.29	−1.88
439.38	7.15	3.86
532.57	7.99	10.22
661.25	8.13	9.01
730.17	7.32	5.68
876.89	6.04	−4.06
920.43	9.98	27.85
1026.92	7.63	8.37
1152.44	6.63	−0.13
1234.60	8.37	14.93
1344.71	7.05	1.22
1426.67	5.63	−11.31
1555.26	8.35	14.23
1741.78	5.97	−6.14
1848.86	5.80	−10.53
1933.75	9.17	22.17
2075.67	7.44	7.35
2319.50	4.39	−24.28

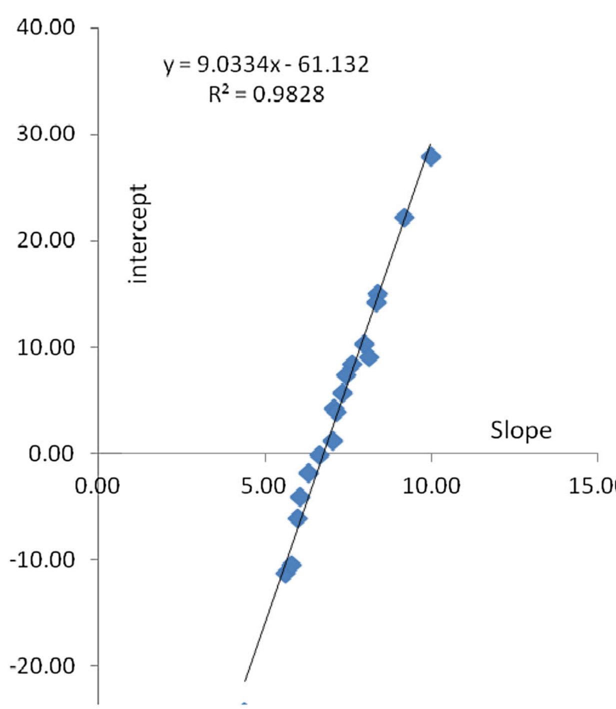

Fig. 3 Slope versus intercept as obtained at different average heights from the plot of $\delta^{18}O$ and δ^2H. Local Meteoric Water Line (LMWL) (Fig. 1a at 1 s) recorded by Geldern et al. 2014 from different average altitudes in the region as per interpretation the original isotopic composition of precipitation as obtained to be $\delta^{18}O = -9.03‰$ and $\delta^2H = -61.13‰$

year 2007, and June for the year 2008. Plotting of $\delta^{18}O$ versus δ^2H has been done to get LMWL lines for each year which is given in Table 7 yearwise.

The slope of these lines and intercept are plotted, as given in Fig. 4 (Table 8), and obtained a straight line; therefore, the isotopic composition of water in precipitation on yearly basis is worked out from this plot to be as per the interpretation by Eq. (2):

$y = 9.50x - 63.66$ or $-63.66 = -9.50x + y$, i.e., $\delta^{18}O = -9.5‰$, $\delta^2H = -63.66$.

All the values and observations in δ^2H and $\delta^{18}O$ are very different for each month and year, as if there is no correlation between them, yet the plot of slope versus intercept is a straight line, which suggests that all the observations are well correlated.

If we multiply $\delta^{18}O = -9.5‰$ with the experimental slope as obtained and add to it the experimental intercept, as given above, we get the value of δ^2H, which is given in Table 9, which can be compared with the observed value, i.e., $\delta^2H = -63.66‰$.

Error in these measurements is ±2.0‰ for δ^2H range, i.e., −65.66 to −66.66‰. All values are within the range which confirms that the isotopic composition of water in precipitation can be taken to be $\delta^{18}O = -9.5‰$ and $\delta^2H = -0.63.66‰$.

Method III: Geldern et al. 2014 had reported δ^2H and $\delta^{18}O$ for water samples from lakes, stream, and springs drawn local water meteoric lines for streams, springs, and

Table 6 Calculated δ^2H values at different mean altitudes

Mean altitude in m.a.s.l.	56.67	206.90	439.38	532.57	661.25	730.17	876.89	920.43	1026.92	
δ^2H	−59.76‰	−58.67‰	−60.70‰	−61.92‰	−64.42‰	−60.41‰	−58.60‰	−62.26‰	−60.52‰	
Mean altitude	1152.44	1234.60	1344.71	1426.67	1555.26	1741.78	1848.86	1933.75	2075.67	2319.50
δ^2H	−59.99‰	−60.65‰	−62.44‰	−62.14‰	−62.17‰	−60.04‰	−63.06‰	−60.63‰	−58.83‰	−63.92‰

Table 7 LMWL Line for different years

Year	LMWL
2003	$\delta^2H = 9.24\delta^{18}O + 23.54‰$
2004	$\delta^2H = 6.56\delta^{18}O + 3.82‰$
2005	$\delta^2H = 8.30\delta^{18}O + 12.36‰$
2006	$\delta^2H = 6.33\delta^{18}O + 2.34‰$
2007	$\delta^2H = 7.67\delta^{18}O + 8.22‰$
2008	$\delta^2H = 6.93\delta^{18}O + 3.07‰$
2009	$\delta^2H = 8.09\delta^{18}O + 18.47‰$

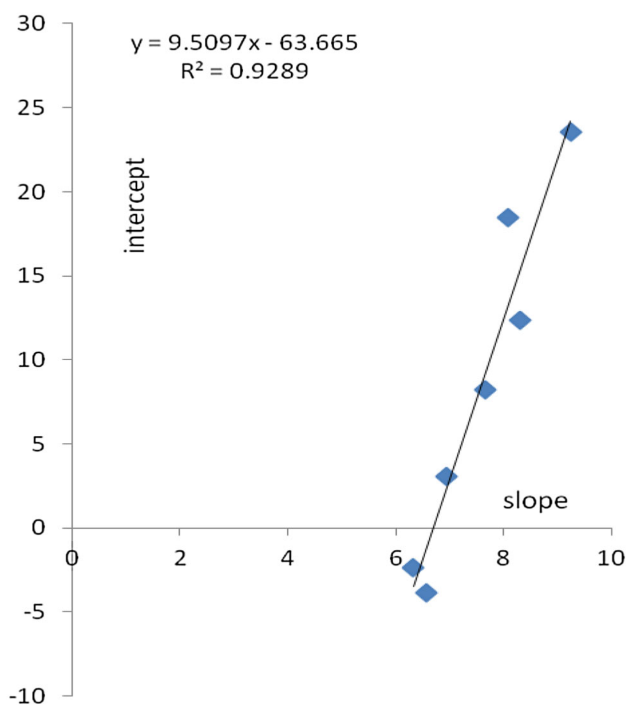

Fig. 4 Showing the plot of slope versus intercept as obtained in different years in May/June 2003–2009 from the plot of $\delta^{18}O$ and δ^2H as recorded in different dates in these years from Fig. 2a–g by Geldern et al. (2014) as per interpretation for the original isotopic composition as obtained is $\delta^{18}O = -9.5‰$ and $\delta^2H = -63.66‰$

lakes and obtained the LMWL for streams, springs, and lakes. The values thus obtained are as follows:For streams $\delta^2H = 7.9(\pm 2)x \quad \delta^{18}O + 10.1(\pm 1.8)‰$,For springs

Table 8 Slope and intercept at different altitudes between 2003 and 2009

Year	Slope (‰)	Intercept (‰)
June 2003	9.24	23.54
May 2004	6.56	−3.82
May 2005	8.3	12.36
May 2006	6.33	−2.34
May 2007	7.67	8.22
May 2008	6.93	3.07
June 2009	8.09	18.47

$\delta^2H = 7.6(\pm 0.5)x \quad \delta^{18}O + 7.9(\pm 4.1)‰$,For lakes $\delta^2H = 5.5(\pm 0.4)x\ \delta^{18}O - 10.5(\pm 3.7)‰$.

Geldern et al. 2014 had defined δp to be the original isotopic composition on the basis of intersection of Local Evaporating Line (LEL) of lakes with Mean Meteoric Water Line (MMWL) for streams and he obtained the value to be $\delta^{18}O = -8.6(\pm 0.2)‰$ and $\delta^2H = -58(\pm 2)‰$. However, plot of slope versus intercept, as given in Fig. 5 (Table 10), resulted in isotopic composition of water from Eq. (2):

$y = 8.87x - 59.54‰ - 59.54 = 8.87x + y$, i.e., $\delta^{18}O = -8.87‰\ \delta^2H = -59.34‰$.

This observed value is the same as obtained by method I and method II earlier.

Conclusion

The isotopic composition by these different methods is from different altitudes in different years and from different surface waters (lake, spring, and stream) as

$\delta^{18}O = -9.03‰\ \delta^2H = -61.13‰$,
$\delta^{18}O = -9.50‰\ \delta^2H = -63.66‰$,
$\delta^{18}O = -8.87‰\ \delta^2H = -59.34‰$.

The error in these measurements is $\delta^{18}O = \pm 0.2‰$ and $\delta^2H = \pm 2.0‰$. The mean value of $\delta^{18}O$ and δ^2H can be taken to be on GMWL.

It is for the first time, these extensive data have been re-analyzed on the basis of precipitation at different altitudes in different years and from different sources of water. The results obtained are within statistical error, and hence,

Table 9 Calculated δ^2H values in different years

Year	2003	2004	2005	2006	2007	2008	2009
δ^2H	−64.25‰	−66.14‰	−64.87‰	−62.37‰	−64.60‰	−62.36‰	−58.38‰

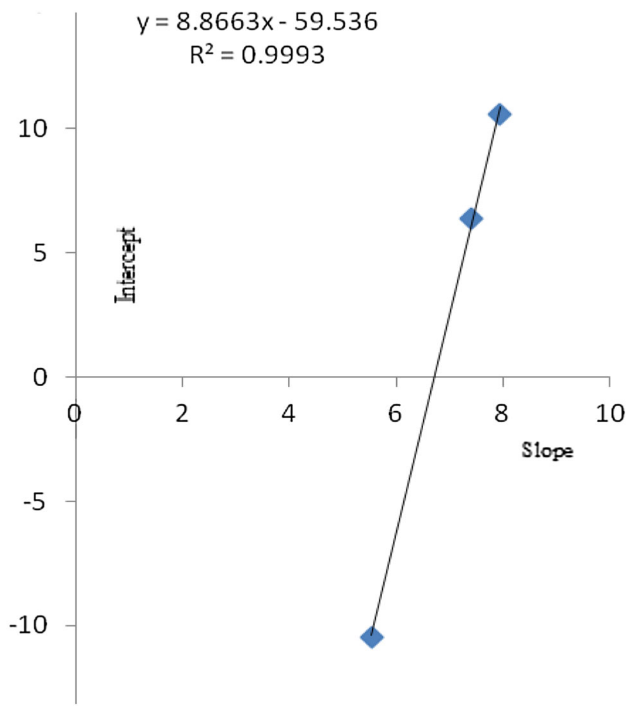

Fig. 5 Plot of slope versus intercept of the LMWL for stream, spring, and lake, giving isotopic composition to be $\delta^{18}O = -8.87$‰ and $\delta^2H = -59.54$‰

Table 10 $\delta^{18}O$ and δ^2H values at different places

Place	$\delta^{18}O$‰	δ^2H‰
Stream	7.94	10.61
Spring	7.4	6.4
Lakes	5.54	−10.49

conclusion can be drawn that the original isotopic composition of water in the formation of clouds and rains had the same origin. It has all happened due to Rayleigh's fractionation which later on gets modified in transit etc due to different environments, e.g., temperature and kinetic fractionation, etc. Process of modification needs to be worked out to get LMWL at different places and locations and transits from the original isotopic composition of water in precipitation.

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